PATENT SPECIFICATION

Inventors: ANTHONY FRANCIS CHILDS and LESLIE THOMAS DOUGLAS WILLIAMS

810,930

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International Classification:—C07f.

COMPLETE SPECIFICATION

Improved process for the Manufacture of Organic Phosphorus Compounds

I, MINISTER OF SUPPLY, London, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of organic phosphorus compounds and particularly concerns a new process for the production of halogen derivatives of alkyl phosphinic acids.

It has been found that, contrary to expectation, tervalent phosphorus compounds containing a halogen atom attached to the phosphorus may be caused to undergo the Arbuzov reaction.

Thus, for example, it has been found that by heating di-isopropyl phosphorofluoridite with methyl iodide it can be converted to monoisopropyl methylphosphonofluoridate. (This compound was formerly sometimes called isopropyl methylfluorophosphinate). Thus, the tervalent phosphorus atom in the starting compound becomes pentavalent and at the same time a direct carbon-phosphorus linkage is established in the product. Products of this type are of considerable importance in connection with the production of organic phosphorus compounds containing halogen some of which are highly toxic substances.

Accordingly, the present invention comprises a process for the manufacture of a mono-alkyl alkylphosphonofluoridate having the formula

$$RO-\overset{\overset{O}{\parallel}}{\underset{\underset{F}{|}}{P}}-R_1$$

(in which R and R_1 mean alkyl radicals which may be similar), wherein a dialkyl phosphorofluoridite, $(RO)_2PF$ is reacted with an alkyl halide or ester, for example an alkyl iodide R_1I, and the mono-alkyl alkylphosphonofluoridate so formed is separated from the products of the reaction.

The reaction may be represented by the following equation:

$$(RO)_2PF + R_1I = RO-\overset{\overset{O}{=}}{\underset{\underset{F}{|}}{P}}-R_1 + RI$$

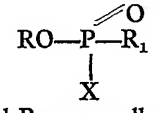
In order that the invention may be readily understood, one form of the process will be described in outline by way of illustrations as follows:

The hitherto unknown compound di-isopropyl phosphorofluoridite $(iso\text{-}PrO)_2PF$ is first prepared, for example, by the interaction of isopropanol and phosphorus dichlorofluoride in the presence of a tertiary base, and after separation and purification is then converted to isopropyl methylphosphonofluoridate by heating with methyl iodide. The main reaction is represented as follows: $(iso\text{-}PrO)_2PF + MeI = Me.PO(iso\text{-}PrO)F + (iso\text{-}Pr)I$. The reaction is not complete at refluxing temperatures but when carried out according to the invention by heating under pressure in a sealed container in a boiling water bath the reaction is substantially complete, giving a good yield of the isopropyl methylphosphonofluoridate which is separated from the reaction mixture by fractional distillation under reduced pressure.

The process of the invention may also be applied to the production of derivatives of alkylphosphinic acids containing a halogen substituent other than fluorine, for example chlorine. The products in this case are alkyl alkylphosphonochloridates which may be produced in an analogous manner.

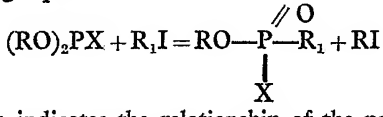
The present invention in its broader aspect therefore provides a process for the manufac-

ture of a mono-alkyl alkylphosphonohalidate having the formula:



(in which R and R_1 mean alkyl radicals which may be similar, and X is fluorine or chlorine,) wherein a dialkylphosphorohalidite having the formula: $(RO)_2PX$ is reacted with a reactive alkyl ester, for example an alkyl iodide, to produce a mixture containing a mono-alkyl alkylphosphonohalidate which is then separated from the products of the reaction.

The process may be represented by the following equation:



which indicates the relationship of the process to the well-known Arbuzov rearrangement.

The following example illustrates one method of carrying the invention into effect.

EXAMPLE:

Production of isopropyl methylphosphonofluoridate.

In the first stage, phosphorus dichlorofluoride is prepared from phosphorus trichloride by the method of Cook et al (J. Chem. Soc. 1949, 2924).

In the second stage, phosphorus dichlorofluoride is distilled into dry ether cooled to 0° C., and the solution added with stirring to a solution of isopropyl alcohol and diethylaniline in dry ether. All the operations are carried out under a stream of dry nitrogen.

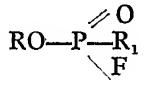
After standing for one hour the solution is warmed to refluxing temperature, cooled and filtered. After removal of the solvent through a 40 cm. helix-packed column, the residue is distilled in vacuo giving a fraction boiling at 49—52° C./53 mm. Redistillation gives a fraction boiling at 52° C./56 mm. which is di-isopropyl phosphorofluoridite, a colourless mobile liquid with a characteristic, rather unpleasant smell.

In the third stage, di-isopropyl phosphorofluoridite (7.4 g.) and methyl iodide (3 ml.) are sealed in a Carius tube, and heated for 7 hours in a boiling water bath. After cooling, the tube is opened and the contents distilled. The main fraction distils at 40—49° C./4 mm. This fraction is contaminated with di-isopropylphosphorofluoridate. Redistillation taking a small middle cut gives 2.7 g. (44%) of pure isopropyl methylphosphonofluoridate.

Although the invention is primarily concerned with the Arbuzov rearrangement in which an alkyl iodide is used, the invention also includes the use of reactive esters other than an alkyl iodide such as dimethyl sulphate, or methyl *p*-toluenesulphonate.

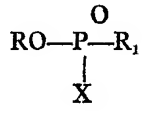
WHAT I CLAIM IS:—

1. Process for the manufacture of a mono-alkyl alkylphosphonofluoridate of the formula:



(in which R and R_1 are alkyl radicals which may be similar), wherein a dialkyl phosphorofluoridite $(RO)_2PF$ is reacted with an alkyl halide or ester, for example an alkyl iodide R_1I, to form the required product which is then separated from the products of the reaction.

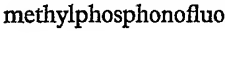
2. Process for the manufacture of a mono-alkyl alkylphosphonohalidate of the formula:



(in which R and R_1 are alkyl radicals which may be similar, and X is fluorine or chlorine) wherein a dialkyl phosphorohalidite

$(RO)_2PX$

is reacted with an alkyl halide or ester, for example an alkyl iodide R_1I, to produce a mixture containing a mono-alkylphosphonohalidate which is then separated from the products of the reaction.

3. Process for the manufacture of isopropyl methylphosphonofluoridate,  , wherein di-isopropyl phosphorofluoridite $(iso\text{-}PrO)_2P.F$ is reacted with a methyl halide or ester by heating under pressure, and the required product then separated by fractional distillation under reduced pressure.

4. Process for the manufacture of isopropyl methylphosphonofluoridate from phosphorus dichlorofluoride substantially as described with reference to the Example.

5. Alkyl alkylphosphonofluoridates whenever produced by a process as hereinbefore particularly described.

W. G. LLEWELLYN,
Chartered Patent Agent,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Improved process for the Manufacture of Organic Phosphorus Compounds

I, MINISTER OF SUPPLY, London, do hereby declare this invention to be described in the following statement:—

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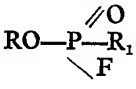

(in which R and R_1 mean alkyl radicals which may be similar) wherein a dialkyl phosphorofluoridite. $(RO)_2PF$ is reacted with an alkyl ester, for example an alkyl iodide R_1I, and the mono-alkyl alkylphosphonofluoridate so formed is separated from the products of the reaction.

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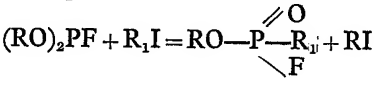

In order that the invention may be readily understood, one form of the process will be described by way of a specific example as follows.

The hitherto unknown compound di-isopropyl phosphorofluoridite $(iso\text{-}PrO)_2PF$ is first prepared, for example, by the interaction of isopropanol and phosphorus dichlorofluoride in the presence of a tertiary base, and after separation and purification is then converted to isopropyl methylphosphonofluoridate by heating with methyl iodide. The main reaction is represented as follows: $(iso\text{-}PrO)_2PF + MeI = Me.PO(iso\text{-}PrO)F + (iso\text{-}Pr)I$. The reaction is not complete at refluxing temperatures but when carried out by heating under pressure in a sealed tube in a boiling water bath the reaction is substantially complete, giving a good yield of the isopropyl methylphosphonofluoridate which is separated from the reaction mixture by fractional distillation under reduced pressure.

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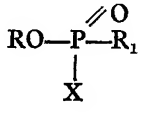
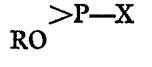


(in which R and R_1 mean alkyl radicals, which may be similar, and X is halogen), wherein a dialkylphosphorohalidite having the formula:



is reacted with a reactive alkyl ester, for example an alkyl iodide, to produce a mixture containing a mono-alkyl alkylphosphonohalidate which is then separated from the products of the reaction.

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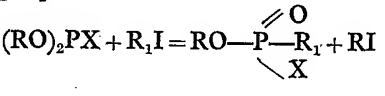

which indicates the relationship of the process to the well-known Arbuzov reaction.

W. G. LLEWELLYN,
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Agent for the Applicant.

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